

The University of Chicago

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ALBITE-ANORTHITE-SPHENE

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY AND PALEONTOLOGY
1941

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THE SYSTEM ALBITE-ANORTHITE-SPHENE

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ABSTRACT

The phase-equilibrium relationships at atmospheric pressure and high temperatures in the systems albite-sphene, anorthite-sphene and albite-anorthite-sphene were studied. The quenching method was used throughout, and the data for the limiting runs in each system are presented. Equilibrium diagrams have been constructed, and the courses of crystallization of typical mixtures under conditions of equilibrium and perfect fractionation are described. The petrological significance of the investigation is discussed with the aid of a tentative quaternary diagram of the system albite-anorthite-diopside-sphene, in which simplified rock compositions occur.

INTRODUCTION

For practical reasons the selection of systems for thermal investigation under conditions of phase equilibrium is ordinarily governed by the stability of the minerals concerned at atmospheric pressure and high temperature. Thus there has been no general investigation of systems in which such important groups of minerals as the amphiboles and micas appear as phases. Abundance of a mineral in nature and its assumed significance in elucidating the complex story of magmatic differentiation also favor its selection as one of the components of a system to be studied. Accordingly, the accessory minerals as a group have not been investigated to any great extent. It must be remembered, however, that they are often diagnostic of a given intrusive body, serving as key minerals in helping to identify the apophyses of the mass and in a sense being comparable to

index fossils. Both fossils and accessory minerals usually represent a small proportion of the rock concerned, yet this is no criterion of their importance. Furthermore various kinds of accessory minerals are characteristic of certain genetic groups of rocks, and investigations of the conditions of their crystallization may well supplement interpretations based on studies of the main constituents of the rock mass.

All three minerals in the present study are well known. Albite and anorthite, comprising the plagioclase series, were selected as typical common and abundant rock-forming minerals whose thermal properties have been determined. Sphene was selected as representing the accessory type, knowing in advance that it acted as a stable component and melted congruently under laboratory conditions.

THE METHOD OF INVESTIGATION

Mixtures were prepared from oxides and carbonates of high purity. Silica was obtained from vein quartz which, after thorough leaching with HCl, contained only 0.03 per cent residue on ignition following treatment with HF and H₂SO₄. A very pure titania, prepared by the Dupont Chemical Company, was used. Alumina was obtained by dehydrating Baker's C.P. Al₂O₃·*x*H₂O. The source of lime in the mixtures was Baker's C.P. precipitated CaCO₃, carefully heated to drive off only the adsorbed water. Soda was added as the anhydrous carbonate, which was obtained by dehydrating Baker's C.P. Na₂CO₃·H₂O.

By mixing weighed amounts of the carbonates and oxides in an agate mortar and fusing several times in a platinum crucible, mixtures of known composition in the form of a homogeneous glass were prepared. Three or more fusions were usually required, and, after each, the charge was removed from the crucible and crushed to a powder in a diamond mortar. Care was taken to remove the particles of steel from the charge with a magnet, before each fusion. The uniformity of the index of refraction of the glass was checked by the immersion method. In color the glass varied from deep amber at the composition of sphene to colorless at the plagioclase join.

The usual equipment and procedure required for the quenching method of thermal investigation, as developed by the Geophysical Laboratory, was used. In general, devitrification of the mixtures prior to making a run in the quench furnace was unnecessary. Calibration of the thermocouples against pure substances was frequently carried out and the necessary corrections made. The calibration materials were: gold, 1,062.6° C.; lithium metasilicate, Li₂SiO₃,

1,201° C.; and diopside, CaMg(SiO₃)₂, 1,391.5° C.

PREVIOUS INVESTIGATIONS
IN THE SYSTEM

THE SYSTEM ALBITE-ANORTHITE

This binary system¹ is one of the three which bound the ternary system under discussion. It shows a complete series of solid solutions from pure albite to pure anorthite, the equilibrium diagram being so familiar that it need not be reproduced here.

THE SYSTEM ANORTHITE-TITANITE

This system was shown by K. Iwase and Y. Saito² to be a simple binary eutectic type, in which the eutectic lies at 62 per cent titanite and 38 per cent anorthite and at a temperature of 1,297° C. In the course of the present study a few mixtures were prepared on the anorthite-sphene join, and liquidus determinations were made. The diagram resulting from this work is shown in Figure 2, and the data from which it was constructed are given in Table 2. The data are in close agreement with those of the earlier investigators, and all due credit for priority is given them, although some minor modifications are suggested by the present work.

THERMAL DATA AND EQUILIBRIUM
DIAGRAMS

THE SYSTEM ALBITE-SPHENE

For each of the binary systems and for the ternary system a table is given showing the composition of the mixture, the

¹ N. L. Bowen, "The Melting Phenomena of the Plagioclase Feldspars," *Amer. Jour. Sci.*, Vol. XXXVIII (4th ser., 1913), pp. 577-99.

² "The Equilibrium Diagram of the System Anorthite (CaO·Al₂O₃·2SiO₂)-Titanite (CaO·TiO₂·SiO₂)," *Science Repts. Tokoku Imperial University*, Vol. XXIII (2d ser., 1934), p. 539.

duration of the run, and the condition of the charge at equilibrium.

The data given in Table 1 have been used to construct the equilibrium diagram for the system (Fig. 1). Points actually determined are shown in solid black dots, representing in most cases

TABLE 1
THERMAL DATA FOR THE SYSTEM
ALBITE-SPHENE

COMPOSITION WEIGHT PER CENT		TIME	TEMPERATURE (CENTIGRADE)	CONDITION AT EQUILIBRIUM
Albite	Sphene			
95.0	5.0	24 hr.	1,127°	A trace of plagioclase in glass; just at the liquidus temperature
92.5	7.5	24	1,127	A trace of sphene and plagioclase in glass; just at liquidus and at the break in the curve
90.0	10.0	60 min.	1,150	Small prismatic sphene crystals in glass
90.0	10.0	30	1,154	All glass
80.0	20.0	60	1,226	Prismatic sphene crystals in glass
80.0	20.0	60	1,232	All glass
70.0	30.0	50	1,270	Sphene crystals in glass
70.0	30.0	50	1,274	All glass
60.0	40.0	60	1,286	Rounded sphene crystals in glass
60.0	40.0	60	1,292	All glass
50.0	50.0	30	1,298	Abundant small sphene crystals in glass
50.0	50.0	30	1,302	All glass
40.0	60.0	35	1,307	Sphene crystals in glass
40.0	60.0	35	1,313	All glass
30.0	70.0	30	1,322	Euhedral sphene crystals in glass
30.0	70.0	30	1,326	All glass
20.0	80.0	30	1,337	Sphene crystals in glass
20.0	80.0	30	1,341	All glass
10.0	90.0	30	1,360	Sphene crystals in glass
10.0	90.0	30	1,364	All glass
0	100.0	10	1,384	Mostly sphene; a trace of glass
0	100.0	20	1,388	All glass

mixtures at successive 10 per cent intervals of composition.

The liquidus curve for the system is shown, passing from 1,386° C., the melting-point of pure sphene, to albite, where the melting-point is 1,118° C., with a break at 92.5 per cent albite. This curve is the temperature-composition boundary, above which all is liquid and below which crystals may exist in equilibrium with liquid. The curve represents a univariant condition throughout most of its length, that is, between sphene and the

break at 92.5 per cent albite. From sphene as far as this point it is a true binary system in which both phases can be expressed in terms of the two components.

From the break in the curve to pure albite, the system is no longer binary, for the break is a little above the melting-point of pure albite. The primary phase in this region is not albite but a plagioclase close to it in composition. The formation of a plagioclase that contains

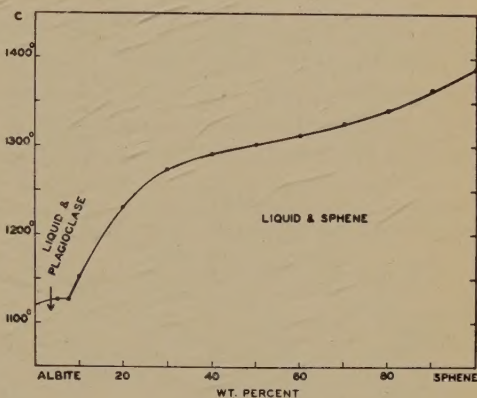


FIG. 1.—The system albite-sphene

even a small amount of lime indicates that the liquid in equilibrium with it has been robbed of some of its lime and that neither composition can be represented in terms of two components.

The equilibrium crystallization of mixtures on the sphene side of the break begins with the formation of sphene crystals. As the temperature falls, the proportion of sphene crystals increases, and the liquid becomes progressively more albitic until it reaches the composition shown by the break in the curve. At this temperature and composition the liquid phase begins to move out of the binary system, as albite-rich plagioclase crystallizes together with sphene. Actually the liquid moves along the extension of the ternary boundary curve beyond

the triangle, but detailed discussion must be postponed until the ternary data have been presented.

A mixture on the albite side of the break begins crystallization with the separation of a plagioclase close to albite in composition, and the liquid immediately moves out of the binary system. The behavior of such mixtures will be made clear when the ternary system is discussed.

THE SYSTEM SPHENE-ANORTHITE

As stated previously,³ this system was studied by other investigators prior to the present work, but minor changes were considered necessary on the basis of the data given in Table 2. From the data

TABLE 2
THERMAL DATA FOR THE SYSTEM
SPHENE-ANORTHITE

COMPOSITION WEIGHT PER CENT		TIME	TEMPERATURE (CENTI- GRADE)	CONDITION AT EQUILIBRIUM
Anorthite	Sphene			
30	70	30 min.	1,314°	Sparse sphene crystals in glass
30	70	30	1,318	All glass
36	64	30	1,303	Rare traces of sphene in glass, hence run is at liquidus
38	62	30	1,304	Many irregular anorthite crystals in glass
38	62	30	1,306	All glass
50	50	30	1,368	A few ragged anorthite crystals in glass
50	50	30	1,372	All glass
70	30	25	1,450	Many euhedral anorthite crystals in glass
70	30	25	1,454	All glass

in this table the equilibrium diagram for the system sphene-anorthite (Fig. 2) was constructed. The eutectic temperature is placed at 1,301° C., which is 4° C. higher than in the earlier study, and the eutectic composition is located at 63 per cent sphene and 37 per cent anorthite, which is 1 per cent closer to sphene. The system is a simple binary eutectic type and shows no unusual features.

³ See p. 2.

THE SYSTEM ALBITE-ANORTHITE-SPHENE

Thermal data and equilibrium diagram.

—In this system a large number of mixtures were made up mostly from the constituent oxides and carbonates, but in some cases they were made up by mixing glasses that had already been prepared. For almost all mixtures, liquidus determinations were made, but, for some, secondary-phase determinations were also made, that is, the temperature was found where the second solid phase began to crystallize. Most of the secondary-phase

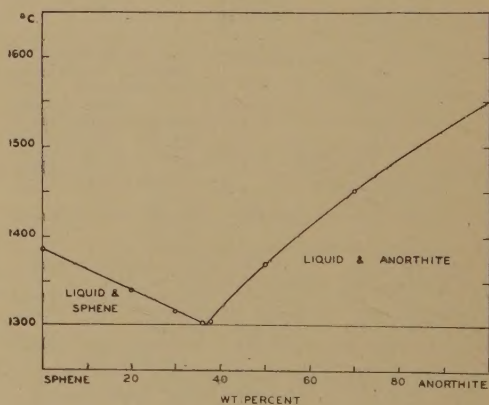


FIG. 2.—The system sphene-anorthite

determinations were made in the part of the diagram where plagioclase is the primary phase (plagioclase field), but a few were made on mixtures lying in the sphene field.

The data given in Table 3 have been used in the compilation of Figure 3, which shows the boundary curve and the isotherms of the liquidus surface. The circles show the compositions of mixtures, both binary and ternary, that have been prepared in the study, most of which were used for liquidus determinations. The system is of a simple ternary nature in all but the 25 per cent of its area, adjacent to the albite-sphene join. Toward the last stages of crystallization, the liquid phase of all mixtures in this

area migrates beyond the limit of the diagram along the extension of the boundary curve. Where this occurs, the liquid phase can no longer be expressed in positive quantities of the three components at the corners of the triangle, but the system remains ternary until such time as a solid phase other than sphene or plagioclase separates from it.

Figure 3 is a projection of a three-dimensional model in which the tempera-

ture axis is perpendicular to the plane of the paper. Such a model would show a single trough descending with increasing gradient from the anorthite-sphene eutectic at *E*, to the break in the curve of the albite-sphene diagram at *F*. In the bottom of the trough is the boundary curve represented by the curved line *EF*, which separates the field of sphene from the field of plagioclase. As used here and throughout this paper, the word "field"

TABLE 3
LIQUIDUS DETERMINATIONS ON TERNARY MIXTURES

	COMPOSITION WEIGHT PER CENT			TIME	TEMPERATURE (CENTI- GRADE)	CONDITION AT EQUILIBRIUM
	Albite	Anorthite	Sphene			
Primary Phase Plagioclase	92.00	4.00	4.00	10 hr.	1,163°	A trace of small euhedral plagioclase crystals; right at liquidus temperature
	86.00	6.00	8.00	5	1,181	Sparse plagioclase crystals in glass
	86.00	6.00	8.00	5	1,185	All glass
	83.00	6.00	11.00	4½	1,169	Plagioclase crystals in glass
	83.00	6.00	11.00	4½	1,173	All glass
	82.00	12.00	6.00	2½	1,243	A trace of plagioclase in glass
	78.50	9.50	12.00	3	1,199	A trace of plagioclase in glass
	75.00	15.00	10.00	45 min.	1,257	A few plagioclase crystals in glass
	75.00	15.00	10.00	45	1,261	All glass
	71.00	13.00	16.00	2 hr.	1,215	A trace of plagioclase crystals in glass
	60.00	30.00	10.00	30 min.	1,349	A trace of plagioclase crystals in glass
	60.00	18.00	22.00	45	1,235	Both plagioclase and sphene crystals in glass
	60.00	18.00	22.00	45	1,239	All glass
	51.25	36.25	12.50	30	1,362	Plagioclase crystals in glass
	51.25	36.25	12.50	30	1,366	All glass
	51.50	28.00	20.50	30	1,300	Plagioclase crystals in glass
	51.50	28.00	20.50	30	1,304	All glass
	43.00	26.00	31.00	30	1,267	Very rare plagioclase crystals in glass
	42.50	42.50	15.00	20	1,380	Plagioclase crystals in glass
	42.50	42.50	15.00	20	1,384	All glass
	33.33	33.33	33.33	35	1,293	Plagioclase crystals in glass
	33.33	33.33	33.33	35	1,297	All glass
	31.25	51.25	17.50	30	1,407	Plagioclase crystals in glass
	31.25	51.25	17.50	30	1,411	All glass
	30.75	30.75	38.50	30	1,278	A few large plagioclase crystals in glass
	30.75	30.75	38.50	30	1,282	All glass
	26.66	46.66	26.66	30	1,373	Plagioclase crystals in glass
	26.66	46.66	26.66	20	1,377	All glass
	16.66	43.33	40.00	30	1,340	Plagioclase crystals in glass
	16.66	43.33	40.00	30	1,344	All glass
	15.00	35.00	50.00	25	1,282	Plagioclase crystals in glass
	15.00	35.00	50.00	25	1,286	All glass
	8.33	56.67	35.00	20	1,404	Plagioclase crystals in glass
	8.33	56.67	35.00	20	1,408	All glass
	7.50	42.50	50.00	30	1,331	Plagioclase crystals in glass
	7.50	42.50	50.00	30	1,335	All glass

TABLE 3—Continued

	COMPOSITION WEIGHT PER CENT			TIME	TEMPERA- TURE (CEN- TI- GRADE)	CONDITION AT EQUILIBRIUM
	Albite	Anorthite	Sphene			
Primary Phase Sphene....	86.90	3.10	10.00	4 hr.	1,155°	Trace of sphene in glass
	78.80	7.20	14.00	2	1,190	Tiny sphene laths in glass
	78.80	7.20	14.00	2	1,194	All glass
	78.00	6.00	16.00	2	1,215	Trace of sphene in glass
	71.00	8.00	21.00	50 min.	1,236	Small sphere crystals in glass
	71.00	8.00	21.00	50	1,240	All glass
	62.00	16.00	22.00	45	1,234	Some sphene crystals in glass
	62.00	16.00	22.00	45	1,238	All glass
	56.50	11.50	32.00	30	1,265	Small euhedra of sphene in glass
	56.50	11.50	32.00	30	1,269	All glass
	46.50	13.00	40.50	30	1,281	Euhedra of sphene in glass
	46.50	13.00	40.50	30	1,285	All glass
	43.00	23.00	34.00	30	1,260	Trace of sphene crystals in glass
	37.50	12.50	50.00	30	1,294	Some sphene crystals in glass
	37.50	12.50	50.00	30	1,298	All glass
	30.00	10.00	60.00	30	1,309	Trace of sphene crystals in glass
	28.00	28.00	44.00	30	1,276	Good sphene crystals in glass
	28.00	28.00	44.00	30	1,280	All glass
	25.71	10.00	64.29	30	1,314	Trace of sphene crystals in glass
	25.00	25.00	50.00	30	1,283	Sphene crystals in glass
	25.00	25.00	50.00	30	1,287	All glass
	20.00	20.00	60.00	30	1,304	Sphene crystals in glass
	20.00	20.00	60.00	30	1,308	All glass
	20.00	5.00	75.00	25	1,331	Sphene crystals in glass
	20.00	5.00	75.00	30	1,335	All glass
	14.00	34.00	52.00	30	1,279	Both sphene and plagioclase crystals in glass
	14.00	34.00	52.00	30	1,283	All glass
	10.00	10.00	80.00	30	1,344	Trace of sphene crystals in glass
	10.00	20.00	70.00	30	1,321	Sphene crystals in glass
	10.00	20.00	70.00	30	1,325	All glass
	7.00	32.00	61.00	30	1,301	Rare sphene crystals in glass

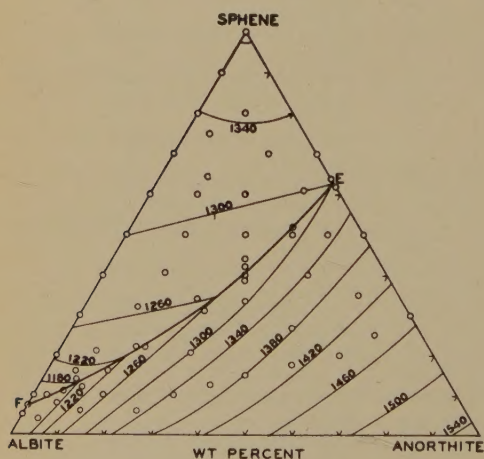


FIG. 3.—The system albite-anorthite-sphene

when applied to a diagram means the portion of the diagram where the phase mentioned is primary.

On each side of the boundary curve the liquidus surfaces rise to maximum points, one at anorthite representing a temperature of 1,550° C., the other at sphene, where the fusion point is 1,386° C. The surface representing the sphene field is relatively flat throughout most of its extent but steepens rapidly on approaching the boundary curve, especially near *F*. The liquidus surface is much steeper in the plagioclase field than in the sphene field, as can be seen from the close spacing of the isotherms.

Degrees of freedom in the system.—

There are no invariant points in the ternary system, because at no composition can three solid phases exist in equilibrium with liquid, as in the case of a ternary eutectic. The complete solid solution of the plagioclases is responsible for this feature, since two mutually soluble solid phases form but one phase, a mix-crystal.

The boundary curve is the locus of points of univariant equilibrium in a condensed system, representing a condition where one liquid and two solid phases can coexist in equilibrium. A point on the boundary curve represents the composition of a liquid which is in equilibrium with sphene and a plagioclase solid solution as defined by a three-phase boundary. The manner in which three-phase boundaries define the composition of the plagioclase in equilibrium at any point will be described later. Thus at a point on the boundary curve only one variable need be fixed in order to define the system. If, for example, a temperature is given at which three phases coexist in this system, the composition is automatically fixed at a definite point on the boundary curve. Conversely, if a composition is stated where three phases are present in equilibrium, the temperature is thereby defined in a condensed system.

Secondary-phase determinations.—In order to understand the system completely, it was necessary to make determinations of the temperatures where the secondary phases began to crystallize from certain mixtures. Most of the mixtures selected had compositions lying within the plagioclase field, since these can be used to find the useful three-phase boundaries in the solid solution field. This type of three-phase boundary is especially important, because, when it is

known, a three-phase triangle for that temperature can be constructed. The significance of the three-phase triangle will be made clear when the courses of crystallization in the ternary system are discussed. In Table 4 the data for the secondary-phase determinations are given.

The data given in Table 4 have been used to construct the three-phase boundaries in the plagioclase field shown in Figure 4. These boundaries may be determined in a number of ways, but in this study the temperature method was used. In order to use this method, the boundary curve must have been determined previously, for each secondary-phase temperature point, necessarily a point on the boundary curve, fixes one end of the three-phase boundary for that temperature.

A section through the diagram following the boundary curve is therefore useful, and such a section with temperature plotted against weight-per cent albite from *E* to *F* is given in Figure 5. The diagram shows a moderately steep but diminishing gradient from *E* to an inflection point near 20 per cent albite, after which it begins to steepen as *F* is approached. Curves of this general shape are characteristic of the fusion surface of the sphene field. The points shown by open circles in Figure 5 are arbitrary intercepts along the boundary curve where temperature and composition were read for plotting the curve.

To each secondary-phase temperature there corresponds a liquid composition which may be stated in terms of weight-per cent albite as shown. These points, once found, may be transferred to the ternary diagram, where they appear as points on the boundary curve. By joining each of them to the point representing the initial composition of the corre-

TABLE 4
SECONDARY-PHASE DETERMINATIONS ON TERNARY MIXTURES

	COMPOSITION WEIGHT PER CENT			TIME	TEMPERA- TURE (CENTI- GRADE)	CONDITION AT EQUILIBRIUM
	Albite	Anorthite	Spene			
Secondary Phase Spene.....	92.00	4.00	4.00	21½ hr.	1,106°	A trace of very small spene crystals with plagioclase in glass
	75.00	15.00	10.00	1	1,181	A trace of spene with abundant plagioclase in glass
	60.00	30.00	10.00	45 min.	1,204	Plagioclase with some spene crystals in glass
	60.00	30.00	10.00	45	1,208	Plagioclase crystals in glass
	51.25	36.25	12.50	45	1,235	A trace of spene with abundant plagioclase in glass
	42.50	42.50	15.00	30	1,246	Abundant plagioclase with a few small spene crystals in glass
	42.50	42.50	15.00	30	1,250	Plagioclase in glass
	31.25	51.25	17.50	30	1,266	Abundant plagioclase with a trace of spene crystals in glass
	26.66	46.66	26.66	45	1,273	Abundant plagioclase with a trace of spene crystals in glass
	20.00	60.00	20.00	30	1,277	A mere trace of spene with abundant plagioclase crystals in glass
Secondary Phase Plagio- clase.....	8.33	56.66	35.00	30	1,285	Abundant plagioclase with some spene in glass
	8.33	56.66	35.00	30	1,289	Abundant plagioclase in glass
	62.00	16.00	22.00	45	1,224	Rare plagioclase crystals with spene in glass
	43.00	23.00	34.00	35	1,250	Rare plagioclase crystals with some spene in glass
	43.00	23.00	34.00	30	1,254	Abundant spene in glass

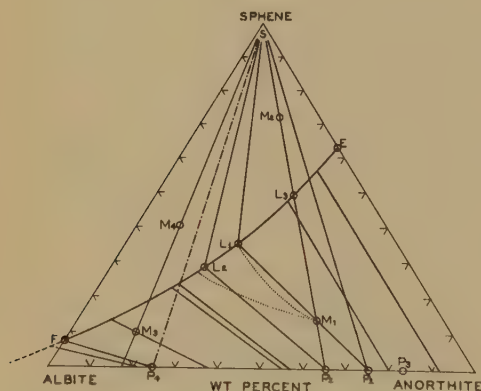


FIG. 4.—The system albite-anorthite-spene, showing the boundary curve and three-phase boundaries in the plagioclase field, with two complete three-phase triangles, SL_1P_1 and SL_2P_2 .

sponding mixture one obtains the appropriate three-phase boundary.

Two complete three-phase triangles have been constructed in Figure 4. These are but two of an infinite number of such triangles that could be constructed over the range of temperatures from E to F along the boundary curve. Each of the triangles constructed indicates the equilibrium condition prevailing at the temperature given by the corner on the boundary curve. The three phases concerned in a particular case are represented in composition by the corners of the triangle. Thus in the triangle SP_1L_1 (Fig. 4) the phases concerned are a plagioclase of composition $Ab_{25}An_{75}$, spene, and liquid as shown by the corner on the boundary curve at L_1 .

Equilibrium crystallization of normal ternary mixtures.—Mixtures lying to the right of the line P_4S are normal ternary mixtures because the compositions of all phases throughout the process of crystallization can be expressed in positive quantities of the components. This area is 75 per cent of the whole triangle. In the plagioclase field a mixture such as M_1 begins to crystallize with the separation of a plagioclase of composition near anorthite, as

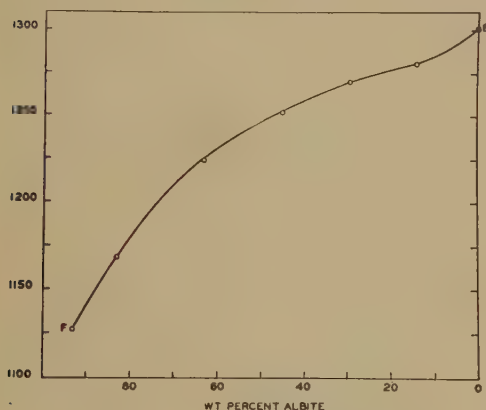


FIG. 5.—Boundary curve section

shown by the tangent to the curve M_1L_1 at M_1 projected to cut the Ab—An join. As cooling and crystallization proceed, the liquid composition changes along a curve such as M_1L_1 , while plagioclase continues to increase in quantity and change in composition toward albite. Under equilibrium conditions all the plagioclase present at any point along the liquid migration curve M_1L_1 has the composition of the plagioclase crystallizing from that particular liquid. The reason for this is that the more anorthitic plagioclase formed earlier in the process is progressively made over through contact with liquid. The plagioclase in equilibrium with liquid L_1 has a composition $Ab_{25}An_{75}$. At this point sphene begins to crystallize, and the liquid is forced to

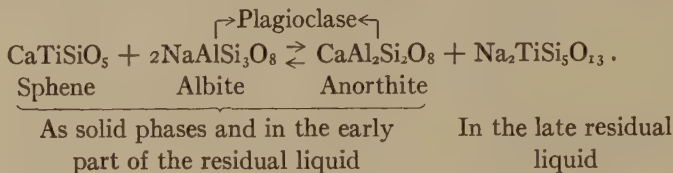
move along the boundary curve, with both solid phases separating. Plagioclase composition continues to change in the direction of albite as liquid follows the boundary curve, and at any temperature the plagioclase composition can be found by interpolating a three-phase boundary from that temperature on the boundary curve. The proportion of phases present can be found by completing the three-phase triangle and by measuring the length of perpendiculars from the point of initial composition to the three sides. When L_2 has been reached, all the liquid has disappeared and the plagioclase has changed to P_2 , $Ab_{35}An_{65}$. The mixture M_1 , now composed of SM_1 parts of P_2 and P_2M_1 parts of sphene, cools without further change in the composition of its constituents.

In the sphene field the equilibrium crystallization of a mixture is much less complicated. A mixture such as M_2 begins to crystallize with the separation of sphene, and the liquid changes composition along a straight line directly away from S . This continues until the liquid reaches L_3 , where plagioclase of composition P_3 begins to form. Liquid composition moves along the boundary curve through L_1 to L_2 , all the plagioclase changing progressively from P_3 to P_2 in composition as it increases in amount. When L_2 is reached, all the liquid has disappeared, and the mixture consists of solid sphene and plagioclase P_2 . The crystallization of any mixture along the line SP_2 gives the same phases, but the relative proportion of the two crystalline phases varies with the position of the mixture on the line.

Equilibrium crystallization of special mixtures.—Mixtures to the left of the line P_4S in an area comprising about 25 per cent of the diagram are somewhat specialized because the last of the liquid

to crystallize has a composition lying on the extension of the boundary curve outside the triangle. Mixtures lying close to the line P_4S within this area can be considered normal throughout most of their course of crystallization, but in the final

equilibrium crystallization is merely sphene and plagioclase. An equation can be written to show the reaction between sphene and albite whereby a plagioclase and a complex hypothetical sodium titanosilicate are formed. This may be



stages, where the liquid passes beyond F , it has a somewhat unusual composition and cannot be expressed in positive quantities of the three components. Liquids lying beyond F are deficient in lime and alumina, because an albitic plagioclase crystallizes in preference to pure albite. This results in an excess of silica, titania, and soda in these liquids, while more than the normal amount of lime and alumina are locked up in the solid phases. Nevertheless, the composition of the liquid phase can be expressed as albite plus sphene minus anorthite, and the system remains ternary until an additional solid phase crystallizes.

A mixture such as M_3 , with a composition lying in the plagioclase field, crystallizes in similar manner to M_1 , following a curved course to the boundary curve where sphene begins to separate. Sphene and plagioclase crystallize together, while the latter is made more albitic through a continuous reaction with the liquid phase. The mixture behaves as a simple ternary one until the liquid phase reaches F , at which time the plagioclase in equilibrium with it is P_4 . Beyond F , sphene and plagioclase continue to form, and the final composition of the solid-solution crystals is about $\text{Ab}_{82.5}\text{An}_{17.5}$. Unless the field of a new phase is encountered between F and the point where all the liquid disappears, the final result of the

considered as an equilibrium reaction between reciprocal salt pairs as in the above formula.

The hypothetical sodium titanosilicate may be considered to decompose to the following known compounds, which, for convenience, we shall refer to as additional phases:



It is probably the field of one of these compounds that the liquid encounters on the extension of the boundary curve. Mixtures in an area of unknown extent close to the albite-sphene join, within the triangle, and on the join from near the break in the curve to sphene itself must give crystals of sphene, a plagioclase, and some of these additional phases before solidification is complete. When the additional phase appears, the system ceases to be ternary. Mixtures near the albite end of the albite-sphene join and in the adjacent area of the ternary diagram will crystallize to an albitic plagioclase of definite composition and the group of additional phases, while sphene itself will not appear as one of the phases.

Within the scope of the present study it was not possible to investigate the equilibrium conditions along the extension of the boundary curve. It was possible, however, to follow the curve beyond the triangle with the solid phase

still plagioclase and not albite. From this fact and from a comparison with more simple but fundamentally analogous systems that have been investigated, the above generalized behavior is indicated.

Perfect fractional crystallization.—Fractional crystallization occurs if solid phases are prevented from reaction with liquid in systems where the solid phase is a mix-crystal or where it possesses an incongruent melting-point. The conditions which cause it are too rapid cooling, the gravitative settling of the solid phase so that it fails to react with liquid, failure to stir the melt, and the zoning of the solid phase in such a way that successive layers of different composition serve as an armor against reaction between the inner zones and the liquid. Only the outermost zone, one of infinitesimal thickness, is in actual equilibrium with liquid at a given instant under conditions of perfect fractionation. Zoning and gravitative separation are the dominant factors in the operation of this principle in nature. Perfect fractionation and perfect equilibrium are the extremes of possible behavior in the cooling melt, and between them lie an infinite number of intermediate methods of crystallization, all included in the term "imperfect fractionation." In fact, the cooling of most mixtures would show intermediate behavior, and only an exact adjustment of conditions could produce either of the extreme forms.

Fractional crystallization of mixtures in the plagioclase field may be discussed with the aid of Figure 4. A mixture such as M_1 on crystallizing under conditions of perfect fractionation shows a course of liquid migration that differs considerably from the curve M_1L_1 , the equilibrium course. At any point on the curved course of perfect fractionation, the solid phase in equilibrium at that instant is

shown by the intercept on the plagioclase join of the tangent at that particular point. The direction of such a course is therefore a curve, starting at M_1 , where the temperature is $1,435^\circ\text{C.}$, and moving across the plagioclase field more nearly parallel to the plagioclase join than the curve M_1L_1 . It finally reaches the boundary curve at a point close to L_2 , and a particular three-phase boundary there is tangent to it. The liquid now follows the boundary curve, as both plagioclase and sphene crystallize together. Since plagioclase has been prevented from reacting with liquid at every stage in the crystallization, the liquid phase persists to a much lower temperature and in greater quantity than when equilibrium conditions prevail. The effect of fractionation is thus to increase the quantity of liquid still present at lower temperatures and to force it toward a more acid composition. On continued cooling the liquid passes beyond F , and at some undetermined temperature other phases in addition to plagioclase and sphene will appear. The nature of these new phases is not definitely known, but suggestions have been made above in discussing equilibrium crystallization of certain mixtures.

With perfect fractionation any mixture in the plagioclase field will yield at least some liquid on the extension of the boundary curve, but if the mixture lies close to the anorthite-sphene join, the amount of this liquid will be almost infinitely small. The amount of such liquid increases as mixtures approach the albite-sphene join.

The fractional crystallization of a mixture such as M_2 in the sphene field begins at a temperature of $1,325^\circ\text{C.}$ with the separation of sphene crystals. The course of crystallization through the sphene field is always a straight line, regardless

of whether the crystals once formed are left in contact with liquid or are removed.

However, when the boundary curve is reached by the liquid phase originating from M_2 , plagioclase of composition P_3 begins to form, and from this point on fractionation will occur if plagioclase crystals fail to be made over by reaction with liquid. The result as before is that liquid composition is offset toward albite and down the temperature gradient.

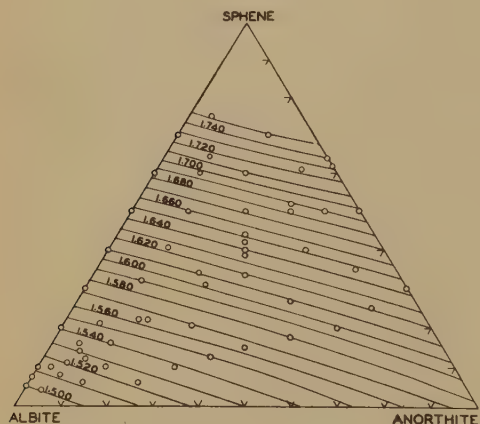


FIG. 6.—The composition-refractive index diagram for glasses.

Starting with M_2 , it is possible for a small quantity of liquid to pass to compositions beyond F . The closer a mixture in the sphene field lies to the albite side of the diagram, the greater is the quantity of liquid of that character that can form.

The composition refractive index diagram.—In Figure 6 the indices of refraction of homogeneous glass mixtures are plotted against weight per cent of the components. Each curve shown in the diagram is the locus of points having the same index of refraction. In making up mixtures, the diagram is very helpful because it offers a rapid method of checking the composition of a given mixture. The glass is finely pulverized and a small sam-

ple of it examined under the microscope for uniformity as shown by the immersion method. When by repeated grinding and fusion the mixture has been rendered uniform, as shown by its refractive index, and the value for the index has been found, it is ready for thermal investigation. The curves of equal refractive index are normally quite smooth and usually approach straight lines. A departure of the index of any glass from the value indicated by the smooth curves suggests that the mixture is off composition.

PETROLOGICAL SIGNIFICANCE

SIMPLIFIED ROCK COMPOSITIONS REPRESENTED IN THE TETRAHEDRON ALBITE-ANORTHITE-DIOPSIDE-SPHENE

In thermal behavior sphene is remarkably similar to diopside, the former having a congruent melting-point at $1,386^\circ\text{C.}$, the latter at $1,391.5^\circ\text{C.}$ In the system albite-anorthite-diopside⁴ the phase diagram is similar to the present system, having two fields separated by a single boundary curve. The system diopside-anorthite is a simple eutectic type, resembling the system sphene-anorthite. The system diopside-albite was considered a simple eutectic type in the above investigation.⁵ More recent work,⁶ however, has shown it to be similar to the system albite-sphene, where there is a break in the curve and not a simple eutectic.

In considering simple systems representative of rock compositions, it is inadequate to deal with sphene and plagioclase alone, and in the present discussion diopside has been included as a nec-

⁴ Bowen, "The Crystallization of Haplobasaltic, Haplodioritic and Related Magmas," *Amer. Jour. Sci.*, Vol. XL (4th ser., 1915), p. 167.

⁵ *Ibid.*, p. 165.

⁶ Personal communication from N. L. Bowen, based on unpublished work by Schairer and Bowen.

essary constituent. It has been shown by Bowen that points near the boundary curve in the system albite-anorthite-diopside have certain analogies with common basic and intermediate igneous rocks.⁷ While it is admitted in the above work that the similarity in composition does not justify the assumption that the crystallization process is identical in the artificial and natural systems, it is pointed out that the trends in the two cases must be very much alike. Certain complications arise in the natural magma which cannot be duplicated under laboratory conditions. These involve the complex nature of the natural crystalline phases and the presence of volatiles. This is acknowledged as a difference which cannot be altogether ignored, but it is considered to have very little effect on the trend of crystallization indicated by laboratory investigations. The dominant parameters governing equilibria of this type are temperature and the composition of the liquid and solid phases, while the pressure plays but a secondary role.

In considering the tetrahedral representation of rock compositions having a small TiO_2 content as the mineral sphene, CaTiSiO_5 , the points concerned must lie within the tetrahedron, but fairly close to the albite-anorthite-diopside face. If we assume the rock to contain 2 per cent TiO_2 , and this is not excessive, we have then a potential source of 5 per cent sphene.

In Figure 7 the points *D* and *B*, respectively, represent a simplified diorite and a simplified basalt composition. At points one-twentieth of the way along lines joining *D* and *B* to the sphene corner, the compositions of the simplified rock types containing 2 per

cent TiO_2 are shown as *D'* and *B'*. This system has been constructed from a knowledge of three of its constituent ternary systems. While no quaternary mixtures were studied in the present investigation, there can be little doubt as to the trend of crystallization within the tetrahedron, even though the exact proportions or compositions of all the phases concerned cannot be stated. The exact location of the quaternary boundary line as well as the position of

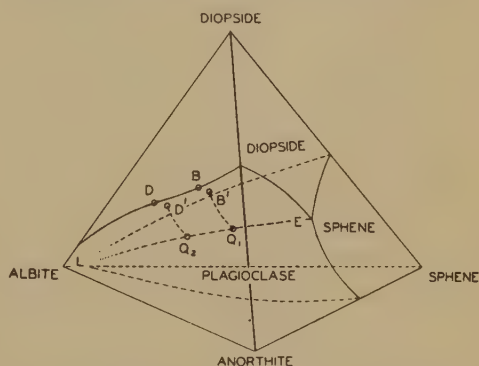


FIG. 7.—The quaternary system, albite-anorthite-diopside-sphene.

the four-phase boundary planes would have to be known in order to work out the composition of the liquid phase and the plagioclase in equilibrium at any time during crystallization. Such a study becomes very complex, but the general behavior of the quaternary system can be readily followed if the ternary type is clearly understood.

CRYSTALLIZATION IN THE QUATERNARY SYSTEM ALBITE-ANORTHITE- DIOPSIDE-SPHENE

The equilibrium crystallization of a mixture such as *B'*, which is suggestive of the average basalt, will begin with the formation of either plagioclase or diopside, depending on the exact location of this point with respect to the diopside-plagioclase boundary surface. Cooling of

⁷ Bowen, "The Crystallization of . . .," *op. cit.*, p. 184.

the mixture causes a migration of the liquid composition toward that boundary surface. When this is reached, the primary phase is joined by the secondary phase, and, as both crystallize, the liquid moves along the boundary surface, following a rather complex course B^1Q_1 , which is a curve upon a curved surface within the tetrahedron. When the quaternary boundary EL is reached, sphene begins to crystallize along with plagioclase and diopside. Very little liquid remains by the time the quaternary boundary is reached, but, on any reasonable assumption as to the position of the curve EL , this liquid is comparatively rich in sphene. The significance of this in the crystallization of actual magmas of the basic type is that sphene should not begin to form, if at all, until the later stages, when the liquid remaining had become fairly concentrated in it, as a result of the earlier separation of pyroxene and plagioclase. It is easy to see that this is true also of a liquid of composition D^1 though not in the same degree, since Q_2 lies at a much smaller sphene concentration than Q_1 . By no possible mechanism can sphene be made to crystallize first from mixtures of these simplified dioritic or basaltic composition. Its behavior would thus be at variance with the common assumption as to the universal early separation of a minor accessory. This fact is, perhaps, of no practical importance in connection with the crystallization of actual gabbroic magmas, for from such magmas TiO_2 separates partly in the form of ilmenite, $FeTiO_3$, and partly in solid solution in pyroxene. The field of sphene is not ordinarily encountered in their crystallization, and no sphene forms unless the crystallization is fractional and the residual liquid is offset toward acidic compositions.

TITANIFEROUS ACCESSORY MINERALS IN THE ACID ROCKS

It is in rocks of granodioritic type that sphene is most abundant, if one overlooks certain rare alkaline rocks such as sphenetite, where it is a major constituent. It is obvious from relations in the tetrahedron that liquid of granodioritic composition must become saturated in sphene at a much lower concentration than basic liquids. In such rocks the total quantity of sphene is ordinarily of the order of 1 or 2 per cent, and it apparently crystallizes early, when the rock is largely liquid. Such behavior would be in entire accord with the findings of the present study.

The mineral rutile TiO_2 , a very common accessory in the granites and to some extent in the diorites, should be mentioned in this connection. In the discussion of the system albite-anorthite-sphene,⁸ an equation was written indicating the type of reaction that must take place near the albite corner of the system. It was pointed out that albite tends to rob the liquid phase of lime and alumina and to favor crystallization as an albitic plagioclase. The same type of reaction must occur in the system albite-anorthite-diopside and also in the more complex quaternary system that has been used to illustrate the behavior of simple rock compositions during crystallization. As shown in the equation there is reason to believe that TiO_2 is released in this reaction, so that one would expect to find the mineral rutile in the late residual product of crystallization along with free quartz and a sodium silicate. The latter is not known as a mineral in igneous rocks, and this might be considered as a weakness in the above argument. However, it must be remembered that in the end-product reactions of magmatic

⁸ See p. 10.

differentiation the hydrous phase which is responsible for vein formation and mineralization begins to assert itself. Sodium silicates are soluble in hot water, in some cases with decomposition, whereby silica is released, and this is adequate to account for the absence of sodium silicates as rock-forming minerals. The suggested reaction may thus be the principal factor in the formation of alkaline solutions from which quartz may form.

The inclusions commonly found in the quartz of granites and pegmatites are of interest in view of the decomposition reaction given.⁹ If we take the products that have been grouped as constituents of the residual liquid, namely, sodium disilicate, rutile, and quartz, an interesting possibility arises. The needle-like inclusions of rutile often found in quartz may have originated from the TiO_2 released in this reaction. It may even be suggested that the accompanying sodium silicate, decomposed by the reaction of water containing chloride ion, may form sodium chloride solution which is imprisoned, upon further growth of quartz, to form brine inclusions.

The rutile grains frequently found in igneous rocks and classed as minor accessories are reputed to be among the first solid phases to crystallize from the molten rock. They are common in the range from diorite to granite composition, and the tendency to develop automorphic outlines is usually considered ample evidence of their priority in crystallization. The present study cannot be called upon to give complete evidence on this point other than to suggest that, in the absence of sufficient lime in the liquid phase of a rock system, rutile will form in preference to sphene. Certainly there is evidence to indicate a generation of rutile at

a very late stage due to the reactions discussed earlier in this section, but petrographic evidence suggests that there may be a much earlier generation of rutile.

The attributed early crystallization of the minor accessory minerals is one of their unusual features and should be accepted with reservation until more evidence is given by actual thermal investigation. When one considers the very low concentration of minor accessories such as rutile, apatite, zircon, etc., in a magma, it is somewhat paradoxical that they should be the first minerals to crystallize. Phase-equilibrium studies show that there is a strong tendency for the constituent with the greatest concentration in a given molten mass to crystallize first, and only when the liquid phase has been enriched in a minor constituent should the latter begin to precipitate. Disparity in the melting-points will counteract this tendency to a certain extent, and it is known that minerals such as albite, having a low melting-point, cause the lowest melting mixture to be drawn relatively close to their own composition. Even so, it is very likely that, in a rock magma, a considerable proportion of the low-melting constituents have formed as solid phases because of their high concentration, before any of the higher melting minor constituents have crystallized. The study of textural relationships and crystal form in thin sections has much to commend it, but it must be admitted that, where an accessory is present with other minerals which are greatly in excess, the relationships seen apply only to the accessory and the grains actually touching it. If, for example, the major constituent is albite and it includes euhedral rutile, we know that the contiguous albite formed after the rutile. This is no proof that all the albite crystals formed after the rutile; in fact,

⁹ See p. 10.

there is very good evidence for believing otherwise. If one takes a simple eutectic diagram with the eutectic drawn over to 95 per cent by weight of the low-melting component and assumes the presence of 2 per cent of the higher melting constituent, simple geometry shows that three-fifths of the entire mixture has crystallized as the low-melting component before any of the high-melting minor constituent begins to form. For this reason

it is wise to be cautious in the interpretation given to the order of crystallization based on the textural relations of the minor accessories.

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